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## (54) MANUFACTURE OF METHYL FORMATE

(71) We, BASF AKTIENGESELLSCHAFT, a German Joint Stock Company of 6700 Ludwigshafen, Federal Republic of Germany, do hereby declare the invention, for which we pray that a Patent may be granted to us, and the method by which it is to be performed to be particularly described in and by the following Statement:—

The present invention relates to an improved process for the manufacture of methyl formate by reaction of methanol with gases containing carbon monoxide.

It is known to manufacture methyl formate by reaction of methanol with carbon monoxide in the presence of alkali metal alcoholates (cf. German Patents 803,046 and 1,046,602). The reaction is usually carried out in bubblers so that the heat of reaction generated can be removed. It is necessary to use pure carbon monoxide for the reaction, but the manufacture of pure carbon monoxide is becoming more and more expensive. According to another process disclosed in German Published Application No. 1,493,058 it is possible to employ gases containing carbon monoxide for the manufacture of methyl formate using packed columns, but the process has the disadvantage that the conversions achieved and consequently the amounts of methyl formate formed are relatively low. Such a process therefore does not lend itself to industrial utilization. In addition, at such low conversions considerable amounts of unreacted methanol must be recovered by distillation. The main disadvantage of the known processes therefore is that either it is necessary to use pure carbon monoxide or only minimum conversions can be achieved.

Hence, the problem with which industry was faced was how to manufacture methyl formate from methanol using gases containing carbon monoxide at conversions which ensure that the process can be utilized industrially.

We have found that the production of methyl formate by reaction of methanol with gases containing carbon monoxide in counter-current flow in a plurality of successive reaction zones at temperatures of 50° to 130°C and at superatmospheric pressure in the presence of alkali metal alcoholates, can be effected more advantageously than hitherto by carrying out the reaction in a column with flooded plates.

The novel process has the advantage that even when gases containing carbon monoxide are used instead of pure carbon monoxide high conversions are achieved, the heat of reaction being removed simply and effectively.

It is advantageous to employ methanol which is as free of water as possible, for example methanol which contains at most 0.1 percent by weight of water.

Gases containing 20 to 90 percent by volume of carbon monoxide are particularly suitable, gases containing 50 to 90 percent by volume of carbon monoxide being preferred. The gases used may contain, in addition to carbon monoxide, other gases which are inert under the reaction conditions, such as nitrogen, hydrogen or methane, and should of course be as free of water as possible.

As a rule, gas rich in carbon monoxide is used in amounts ranging from 0.5 to 20 Nm<sup>3</sup> per kg of methanol.

The reaction is carried out at temperatures of 50° to 130°C. Particularly good results are obtained at temperatures of 70° to 120°C. As a rule, the reaction is carried out at a pressure of from 40 to 300 atmospheres. It is advantageous to so select the pressure that a carbon monoxide partial pressure of 40 to 150 atmospheres, especially of 60 to 110 atmospheres, is maintained.

The reaction is carried out in the presence of an alkali metal alcoholate. Sodium

methylate and potassium methylate, especially the former, have proved to be particularly suitable. The said alcoholates are advantageously used in an amount of from 0.4 to 1.5 percent by weight based on the methanol employed.

The reaction is carried out in a column with flooded plates by passing the methanol and the gas containing carbon monoxide through the column countercurrent to one another.

Examples of suitable columns are bubble-cap tray columns, valve-tray columns or tunnel-cap tray columns. It is advantageous to use columns with 5 to 60 trays, especially if it is desired to remove most of the carbon monoxide from the gas mixture used. On the other hand, 5 to 15 plates suffice if it is only desired to remove part of the carbon monoxide from the starting mixture. Columns with flooded plates which are so designed that the individual plates can be cooled are of particular industrial importance. This is achieved, for example, by providing pipes or pipe coils, through which water flows, on the individual plates.

The reaction is advantageously carried out in such a way that a methyl formate content of 20 to 70 percent by weight, especially of 30 to 60 percent by weight, is maintained at the point at which the liquid reaction mixture leaves the column, for example the bottom of the column, when columns with flooded plates are used.

The columns with flooded plates are advantageously operated on the principle of a gas scrubber, i.e. methanol is introduced at the top whilst the gases containing carbon monoxide are introduced at the bottom, thus flowing countercurrent to the methanol. The mixture containing methyl formate is withdrawn from the bottom of the column. Pure methyl formate can be isolated simply from the mixture by distillation.

It has also proved advantageous to maintain dwell times for the liquid phase of 50 to 1,500 seconds, especially 300 to 1,000 seconds, when carrying out the reaction.

Furthermore, it has proved particularly advantageous to introduce the catalyst into the column two to five plates below the point at which the methanol is added.

The process according to the invention is not only suitable for the manufacture of methyl formate but also for the simultaneous production of synthesis gases containing carbon monoxide, for example by using as the starting gas mixture a gas which has a relatively high carbon monoxide content and reducing it to a certain level by the process of the invention. For example, synthesis gas mixtures suitable for the manufacture of methanol can be produced in this way.

Methyl formate which has been produced by the process of the invention can be used,

for example, for the manufacture of formamide and dimethylformamide, which are important solvents and starting materials for further syntheses.

The invention is further illustrated by the following Examples.

#### EXAMPLE 1

A column with 8 cooled bubble-cap trays is used for carrying out the process. 30 l of methanol containing 0.7 percent by weight of sodium methylate is introduced hourly at the top of the column. A gas mixture of 51 percent by volume of hydrogen and 49 percent by volume of carbon monoxide is introduced at a rate of 33 Nm<sup>3</sup>/hour below the bottom plate. A temperature of 80°C and a pressure of 300 atmospheres are maintained in the column. This corresponds to a carbon monoxide partial pressure of 1.47 atmospheres. The dwell time of the liquid phase is 350 seconds. 17Nm<sup>3</sup> of gas containing 23 percent by volume of carbon monoxide are obtained hourly at the top of the column. The reaction product withdrawn from the bottom of the column contains 65 percent by weight of methyl formate. The gas which is obtained at the top of the column is suitable for the manufacture of methanol using oxide catalysts

#### EXAMPLE 2

30 l of methanol containing 0.7 percent by weight of sodium methylate is introduced hourly at the top of a bubble-cap tray column with 15 cooled plates. 29 Nm<sup>3</sup> of a gas containing 49 percent by volume of carbon monoxide and 51 percent by volume of hydrogen is introduced hourly, at a pressure of 100 atmospheres, below the bottom plate. The carbon monoxide partial pressure is 49 atmospheres and the dwell time of the liquid phase is 650 seconds. A temperature of 80°C is maintained in the column. 20 Nm<sup>3</sup> of gas containing 29 percent by volume of carbon monoxide are withdrawn hourly at the top of the column, whilst the reaction product withdrawn from the bottom of the column contains 43 percent by weight of methyl formate. The gas obtained at the top of the column is suitable for the manufacture of methanol.

#### EXAMPLE 3

The procedure of Example 1 is followed except that a column with 30 cooled bubble-cap trays is used and 22.7 Nm<sup>3</sup> of a gas containing 49 percent by volume of carbon monoxide and 51 percent by volume of hydrogen are introduced hourly at a pressure of 300 atmospheres to the bottom plate. The dwell time of the liquid phase is 900 seconds. 12 Nm<sup>3</sup> of gas containing 5 percent by volume of carbon monoxide are obtained hourly at the top of the column, whilst

the reaction product, which contains 54 percent by weight of methyl formate, is withdrawn from the bottom of the column.

5 WHAT WE CLAIM IS:—

1. A process for the manufacture of methyl formate by reaction of methanol with a gas containing carbon monoxide in counter-current flow in a plurality of successive  
10 reaction zones at a temperature of 50° to 130°C and superatmospheric pressure in the presence of an alkali metal alcoholate, wherein the reaction is carried out in a column with flooded plates.  
15 2. A process as claimed in claim 1, wherein the reaction is carried out in a column with flooded and cooled plates.  
3. A process as claimed in claim 1 or 2, wherein a residence time of 50 to 1,500  
20 seconds is employed.  
4. A process as claimed in any of claims 1 to 3, wherein a content of 20 to 70 percent by weight of methyl formate is maintained in the reaction mixture at the point at which  
25 the liquid reaction mixture leaves the column.  
5. A process as claimed in any of claims

1 to 4, wherein the alkali metal alcoholate is introduced two to five plates below the point at which the methanol is introduced. 30

6. A process as claimed in any of claims 1 to 5, wherein a carbon monoxide partial pressure of 40 to 150 atmospheres is maintained.

7. A process as claimed in any of claims 35 1 to 6, wherein the carbon monoxide-containing gas contains 50 to 90 percent by volume of carbon monoxide.

8. A process as claimed in any of claims 1 to 7, wherein a column having 5 to 60  
40 plates is employed.

9. A process for the manufacture of methyl formate carried out substantially as described in any of the foregoing Examples.

10. Methyl formate when manufactured 40 by a process as claimed in any of claims 1 to 9.

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